194 *J. Phys. Chem. A* **2004,** *108,* 194−202

Aromatic vs Diradical Character in the Transition States of the Cope Rearrangements of 1,5-Hexadiene and Its Cyano Derivatives

Joshua J. Blavins,[†] David L. Cooper,*[‡] and Peter B. Karadakov*[†]

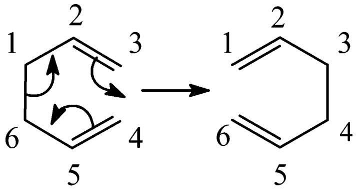
Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K., and
Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, U.K.

Received: September 5, 2003; In Final Form: October 23, 2003

Using geometries optimized at the (U)B3LYP/6-31G(d) level, ab initio modern valence bond calculations are used to quantify directly the relative importance of aromatic, diradical, and bisallyl contributions to the transition states of gas-phase Cope rearrangements of 1,5-hexadiene and various cyano derivatives. The main effect on the character of the transition state of substituting radical-stabilizing cyano groups is found to be indirect, via the geometry, with shorter interallyl separations favoring diradical character and larger ones favoring aromaticity. In the case of the parent Cope reaction, the weights of the aromatic and diradical components are comparable at the transition state. We find that bisallyl character only becomes important for transition states with rather large interallyl separations.

Introduction

The Cope rearrangement of 1,5-hexadiene is the thermally allowed [3,3]-sigmatropic rearrangement that might conventionally be represented by the scheme



in which the curly arrows signify the supposed movement of electron pairs, and we have added a convenient numbering scheme for the carbon atoms. There has been a great deal of theoretical and experimental work to determine the actual mechanism,[1−21] including various suggestions that it might involve consecutive steps via a diradical intermediate. The consensus now is that the reaction actually proceeds through a chairlike C_{2h} transition state, in which the bond-breaking and bond-making processes are simultaneous.

The transition state (TS) lies on a relatively flat potential-energy hypersurface, such that the inclusion of dynamic electron correlation is essential in order to obtain a reliable geometry. The latter is especially important because of the sensitivity of the nature of the TS to the interallyl distance. Calculations at just the "six electrons in six orbitals" CASSCF level, which we denote CAS(6,6), suggest an "aromatic" TS with a C1−C6 separation of $R_1 \sim 2.2$ Å, which is rather too large. Instead, higher-level calculations indicate values of R_1 in the vicinity of 1.9 Å. Probably the most reliable value of R_1, 1.902 Å, comes from the extended-basis highly correlated treatments reported by Ventura and coauthors.[20] Calculations at the CAS(6,6) level suggest also a stable cyclohexane-1,4-diyl intermediate at short R_1, around 1.6 Å, but this is not reproduced by higher level calculations. Borden and Davidson[9] identified the Cope rearrangement as a system for which even qualitatively meaningful results required the inclusion of dynamic correlation.

The shortcomings of various wave functions and basis sets for the description of the Cope rearrangement of (substituted) 1,5-hexadiene have been discussed by Staroverov and Davidson.[6] Those authors found good agreement between experimental and CASPT2N results. For a C_{2h} cut through the potential-energy hypersurface, varying the interallyl distance, the same authors found that the extent of the diradical character, as measured by the density of effectively unpaired electrons, tends to a minimum near the TS.[6,16,17] Their DFT calculations located chairlike C_{2h} (or C_s) saddle points for various substitution patterns, with activation enthalpies that are in good agreement with values derived from experiment (see particularly ref 6 and references therein). Unfortunately, unrestricted DFT calculations tend to produce spurious intermediates at short interallyl separations, typically around 1.6−1.7 Å, that cannot be found by means of appropriate spin-restricted calculations.[6,17]

The effect of substituents on the nature of the TS has been studied extensively.[3,6,12,13,16−18,21] In particular, Doering and Wang[13,18] described two general types of transition region, depending on the substituents at the four "active" (C1, C3, C4, and C6) positions and on those at the two "nodal" (C2 and C5) positions. In their "chameleonic" model, radical-stabilizing perturbations at the active positions shift the lowest-energy chairlike C_s TS toward two noninteracting allyl radicals, whereas radical-stabilizing perturbations at the nodal positions shift it toward a cyclohexane-1,4-diyl diradical. The chameleonic model is meant to apply when the two allyl moieties contain substituents of the same type, so that the stabilization effects can in principle act cooperatively. On the other hand, in the case of competitive or conflicting effects, arising from different types of substituent in the two allyl moieties, the "centauric" model is meant to be more appropriate, with a transition region envisaged as a partially diyl, partially bisallyl hybrid.

The effects of cyano substitution on the Cope rearrangement TS have been studied by Hrovat et al.[12] who did indeed show

---

* To whom correspondence should be addressed. E-mail: dlc@liverpool.ac.uk (D.L.C.); pbk1@york.ac.uk (P.B.K.).
[†] University of York.
[‡] University of Liverpool.

10.1021/jp036660i CCC: $27.50

via DFT calculations that energetic effects, as well as geometrical effects, are cooperative in the chameleonic model and competitive in the centauric model. Staroverov and Davidson[6,17] examined the effects of cyano substitution using an isodesmic reaction approach and found that cyano groups at C1, C3, and C5 provide a nearly additive stabilization of each point along the C_s cut but with a competitive effect on the geometry. By use of the density of effectively unpaired electrons, they showed that the radical character of the TS is not significantly altered by the presence of radical-stabilizing substituents but that it depends instead mostly on the interallyl distance. This stresses, once again, the overwhelming importance of the interallyl distance, which can be seriously overestimated by approaches such as CAS(6,6) that do not take proper account of dynamic correlation. On the other hand, provided that TS geometries are determined at a suitable higher level of theory, it turns out to be meaningful to examine information derived from CAS(6,6) calculations carried out in the general vicinity of the TS.[6,16,17] The same would not be true of analysis carried out at the geometries derived from CAS(6,6) calculations.

The present study follows closely from the work by Staroverov and Davidson,[6,16,17] in which they considered the parent 1,5-hexadiene system as well as various multiply substituted cyano derivatives that might provide good examples for the chameleonic and centauric models. We use much the same level of theory for optimizing the transition-state structures but then use ab initio valence bond (VB) calculations to obtain *directly* quantitative information about the relative importance of different structures and, especially, the key modes of spin coupling. Previous work has in general tended to infer this type of information from other observations. We employ so-called modern VB wave functions which, in the present case, are essentially of CAS(6,6) quality.

An alternative strategy could be to re-express CAS(6,6) wave functions in the basis of orbitals localized according to the Boys criterion, such as in CiLC (configuration interaction, localized molecular orbital, CASSCF) studies.[21] Very recently, Blancafort et al.[22] have also reported results based on localized orbitals, analyzing a CAS(6,6) wave function for the 1,5-hexadiene TS by means of the elements of an appropriate spin-exchange matrix. Of course, it is crucial that any such analysis be carried out with appropriate interallyl separations rather than with those derived only from CAS(6,6) geometry optimizations.

Computational Procedure

Following the work of Staroverov and Davidson,[6,16,17] we optimized TS geometries for 1,5-hexadiene (1,5-H), 1,3,5-tricyano-1,5-hexadiene (1,3,5-TCH), and 1,3,4,6-tetracyano-1,5-hexadiene (1,3,4,6-TeCH) at the UB3LYP level (unrestricted DFT with the popular B3LYP hybrid[23] functional) using a large integration grid consisting of 99 radial shells and 974 angular points per shell and with the 6-31G(d) basis set. We carried out analogous calculations for 2,5-dicyano-1,5-hexadiene (2,5-DCH) at the B3LYP/6-31G(d) level because it has been shown that the TS only exists on the spin-restricted potential-energy hypersurface.[17] The TS geometries, which met the tight convergence criteria for optimizations with Gaussian 98,[24] were confirmed via analytical Hessians as first-order saddle points on the corresponding energy hypersurfaces. It is true that DFT calculations with hybrid functionals can lead to spurious minima for sigmatropic rearrangements,[6,17] but we are dealing here only with the TS geometries.

The final UB3LYP/6-31G(d) wave functions for the 1,5-H, 1,3,5-TCH, and 1,3,4,6-TeCH TSs were in fact observed to be of the restricted type, with $\langle S^2 \rangle = 0$, just as was reported in ref 17, and so we may label these results simply as B3LYP/6-31G(d). We carried out stability analyses,[25] in order to gain a better understanding of the interplay between restricted and unrestricted solutions, and found that the restricted B3LYP/6-31G(d) wave functions for all four systems, 1,5-H, 2,5-DCH, 1,3,5-TCH, and 1,3,4,6-TeCH, are singlet stable at the TS geometries. Additionally, the B3LYP/6-31G(d) TS wave functions for 1,5-H, 1,3,5-TCH, and 1,3,4,6-TeCH were also found to be triplet stable, in keeping with the observation that UB3LYP/6-31G(d) geometry optimizations converge to restricted wave functions. However, we observed triplet instability of the B3LYP/6-31G(d) solution for the TS of 2,5-DCH; this is, of course, closely related to the previously mentioned absence of a TS on the UB3LYP/6-31G(d) potential-energy surface, and it also suggests that a more accurate geometry optimization of the TS for the Cope rearrangement of 2,5-DCH may require a much higher level of theory.

VB calculations were carried out at the optimized TS geometries, within the 6-31G basis set. In the present work, we use spin-coupled (SC) wave functions based on a single spatial configuration consisting of N fully optimized, nonorthogonal, one-electron "active" orbitals ψ_μ, together with a set of n fully optimized, orthogonal, doubly occupied "inactive" orbitals ϕ_i. Whereas the orbitals in classical VB approaches are typically restricted to be rather localized, by expanding each of them only in basis functions located on a particular atomic center, no such restrictions were imposed here on any of the orbitals (active or inactive). It is usual to use the appellation "modern" valence bond when orbitals are entirely free to deform toward, and to delocalize onto, other centers. For each system, the SC(6) wave function takes the form[26]

$$\Psi = \hat{A}\Big(\big(\prod_{i=1,n} \phi_i \alpha \phi_i \beta\big)\big(\prod_{\mu=1,N} \psi_\mu\big)\Theta^N_{SM}\Big)$$

in which the active-space spin function Θ^6_{00} for $N = 6$ electrons, with total spin $S = 0$ and projection $M = 0$, is expanded in the full spin space[27] of $f^6_0 = 5$ functions $\Theta^6_{00;k}$

$$\Theta^N_{SM} = \sum_{k=1}^{f^N_S} C_{Sk}\Theta^N_{SM;k}$$

The variational parameters, namely the spin-coupling coefficients (C_{Sk}) and the coefficients of the active (ψ_μ) and inactive (ϕ_i) orbitals in the underlying 6-31G basis set, are optimized simultaneously. As has been well documented, such very compact SC(6) wave functions should be only very slightly inferior to the corresponding CAS(6,6) description but they are, of course, a great deal simpler to interpret directly in terms of familiar chemical concepts.

The SC(6) calculations presented here were performed using a version of our code[28] which works in the Kotani spin basis.[27,29] Of course, it is more convenient for discussions of changes in the active-space spin-coupling patterns of these systems to transform instead to the Rumer basis.[27,30] The (exact) interconversion between different bases of spin eigenfunctions was carried out through a specialized code for symbolic generation and manipulation of spin eigenfunctions, SPINS.[31] The five linearly independent Rumer functions $\Theta^6_{00;k}$, which span the complete space for six electrons coupled to an overall singlet, are identified in Figure 1. Rumer functions 1 ≡ (1−2, 3−4, 5−6) and 4 ≡ (1−6, 2−3, 4−5) are, of course, reminiscent of the traditional Kekulé structures for benzene, and they account for the "aromatic" character. The three remaining Rumer

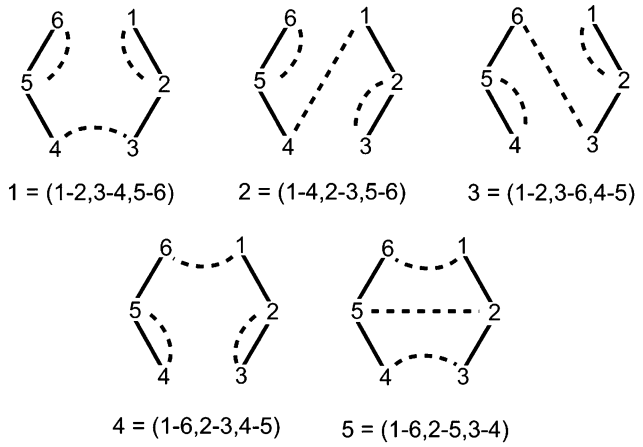


Figure 1. Rumer spin eigenfunctions included in the active-space spin-coupling pattern Θ_6^{00}.

functions correspond to Dewar-like structures. More specifically, it is the function 5 ≡ (1−6, 2−5, 3−4) which describes the "diradical" component, whereas the functions 2 ≡ (1−4, 2−3, 5−6) and 3 ≡ (1−2, 3−6, 4−5) correspond to the "bisallyl" character. It is thus by examining the total spin function, expressed in the Rumer basis, that we can obtain directly quantitative information about the actual relative importance of the aromatic, diradical, and bisallyl contributions.

One of the simplest and most widely used schemes for assessing the importance of particular modes of spin coupling within the total spin function is the one due to Chirgwin and Coulson.[32] Simply by restricting one of the summations in the normalization condition for the total spin function, Chirgwin−Coulson weights P_k^{CC} may be defined according to

$$P_k^{\mathrm{CC}} = C_{Sk}\sum_{l=1}^{f_S^N} C_{Sl}(\mathbf{S})_{kl}$$

in which $(\mathbf{S})_{kl} = \langle \Theta_{SM;k}^{N} | \Theta_{SM;l}^{N} \rangle$. One disadvantage of this approach is that although the weights must add to unity, individual values of P_k^{CC} are not guaranteed to lie in the range 0−1. Even though this proved not to be a problem in the present work, we chose also to examine weights defined according to the inverse−overlap scheme of Gallup and Norbeck[33]

$$w_k^{\mathrm{GN}} = (C_{Sk})^2/(\mathbf{S}^{-1})_{kk}$$

Simple rescaling of these w_k^{GN} quantities, so as to have a sum of unity, gives the required Gallup−Norbeck weights P_k^{GN}, each of which is restricted to the range 0−1. Chirgwin−Coulson weights (unlike those from the Gallup−Norbeck scheme) are linear, in the sense that the total weight of (say) the "aromatic" component is simply the sum of the corresponding weights for Rumer functions 1 and 4.

We also carried out SC calculations for 1,5-hexadiene using the 6-31G(d) basis set. We found that the differences in the orbital plots, overlap integrals, and spin-function weights were sufficiently small that the 6-31G basis should be sufficient for our present purposes.

Results and Discussion

The Cope Rearrangement of 1,5-H. Our B3LYP/6-31G(d) geometry for the lowest-energy chairlike C_{2h} TS in the Cope rearrangement of 1,5-H is shown in Figure 2a, together with the corresponding very similar B3LYP/6-31G(d) structural parameters of Hrovat and coauthors.[12] Our interallyl distance, as measured by the C1−C6 separation of R_1 = 1.9661 Å, is of course the same as that reported by Staroverov and Davidson.[17] The key features of the active orbitals from SC(6)/6-31G calculations at this geometry can be seen from Figure 2b. Although no such restrictions were imposed during the calculations, we observe that the final SC orbitals, which are a unique outcome of the optimization procedure, are fairly localized and permute into one another under symmetry operations of the molecular point group. For each system where this occurs, we have numbered the orbitals in a consistent fashion according to the carbon atoms with which they are mostly associated such that (running clockwise) ψ_1, ψ_2, and ψ_3 are in one allyl moiety and ψ_4, ψ_5, and ψ_6 are in the other.

The high symmetry means that this particular system has just two symmetry-unique SC orbitals (e.g., ψ_1 and ψ_2), and this is of course reflected in the matrix of SC orbital overlap integrals, given in Table 1, which features many repeated values. These quantities will be discussed later. Orbitals ψ_1 and ψ_6 (and similarly ψ_3 and ψ_4) correspond to the forming/breaking carbon−carbon σ bonds. Orbital ψ_2 (or similarly ψ_5) is located on the central carbon atom of one of the allyl moieties and participates in the synchronous π bond breaking and π bond making processes that also involve orbitals ψ_1 and ψ_3 (or ψ_4 and ψ_6).

The Chirgwin−Coulson (P_k^{CC}) weights of the Rumer spin functions included in the SC(6) active-space spin-coupling pattern Θ_{00}^{6} are given in Table 2. The two Kekulé-like modes have equal weights by symmetry, of 0.21, so that the total "aromatic" weight is 0.42. However, the largest single component, due to the final Rumer function, corresponds to a "diradical" weight of 0.46. The total weight of the minority, bisallyl, contribution is just 0.12. Contrary to some expectations of a predominantly aromatic TS, we find roughly equal aromatic and diradical components in the SC(6) wave function.

As shown in Table 2, the Gallup−Norbeck weights (P_k^{GN}) for the individual Rumer functions suggest a much greater preponderance of the diradical mode. On the whole, though, values of P_k^{GN} do tend to show a strong bias toward the largest contributor to the total spin function. Nevertheless, the high value of P_5^{GN} does suggest that the relatively high Chirgwin−Coulson weight for this "diradical" mode is not some sort of artifact of the Chirgwin−Coulson scheme.

As mentioned earlier, it is the interallyl distance (R_1) that plays a key role in determining the character of the TS. So, to investigate the influence of R_1 on the active-space spin-coupling pattern, we performed a series of SC(6)/6-31G calculations at TS geometries fully optimized at different levels of theory (but always with the same 6-31G(d) basis set). The methods employed, with the corresponding value of R_1 in brackets, were MP2(Full) (1.783 Å), MP4(Full, SDQ) (1.858 Å), QCISD(Full) (1.871 Å), B3LYP (1.966 Å), and CAS(6,6) (2.192 Å). The resulting total Chirgwin−Coulson weights are plotted against R_1 in Figure 3 where, as before, "aromatic" labels the combination 1 ≡ (1−2, 3−4, 5−6) plus 4 ≡ (1−6, 2−3, 4−5), "diradical" signifies 5 ≡ (1−6, 2−5, 3−4), and "bisallyl" relates to the minority component, 2 ≡ (1−4, 2−3, 5−6) plus 3 ≡ (1−2, 3−6, 4−5). Drawing smooth curves through these points would require data for further geometries, but the general form of the dependence on R_1 is already sufficiently clear. For the shortest value of R_1 considered here, it is the diradical character that dominates, with a weight of 0.64. As R_1 increases, the aromatic character increases at the expense of the singlet diradical component. At the (preferred) geometry from the

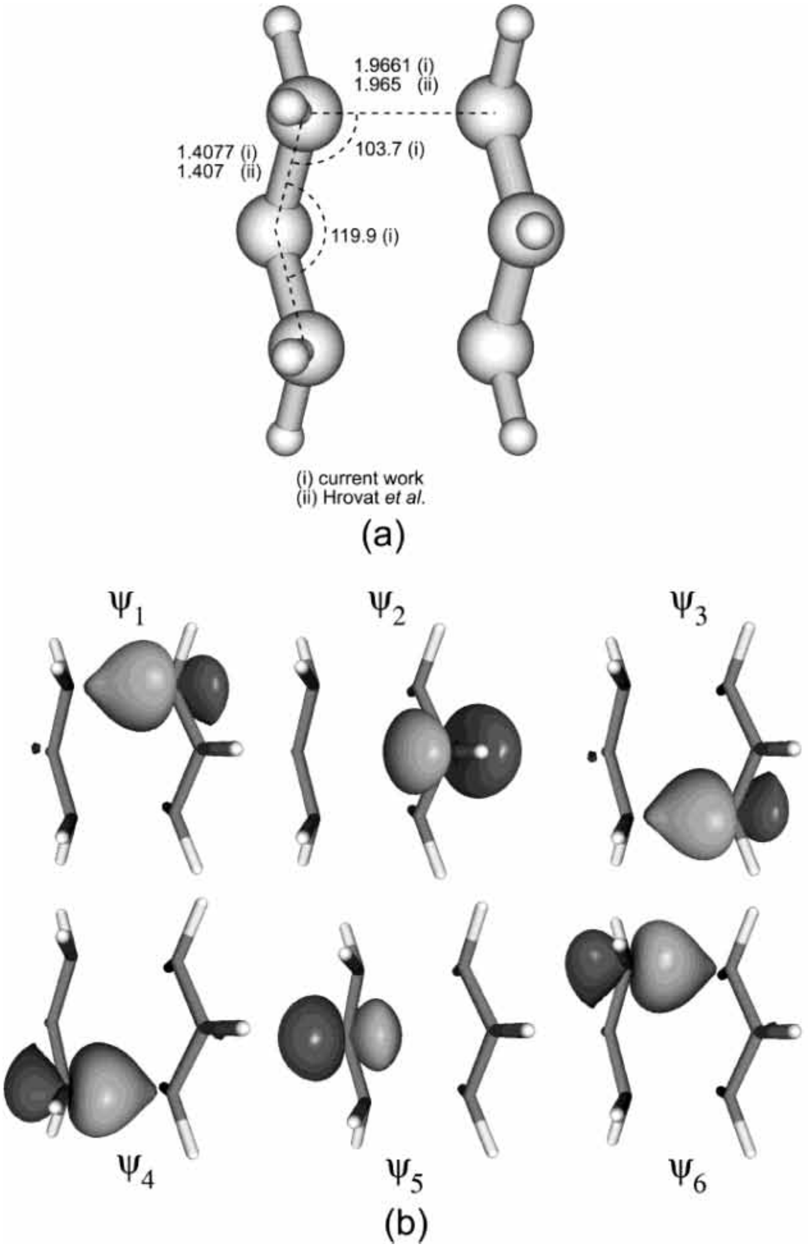


Figure 2. (a) B3LYP/6-31G(d) geometry for the gas-phase TS of the Cope rearrangement of 1,5-hexadiene, with bond lengths in angstroms, angles in degrees. (b) Active orbitals from SC(6)/6-31G calculations at this geometry; three-dimensional isovalue surfaces corresponding to $\psi_\mu = \pm 0.1$ were drawn from the virtual reality modeling language files produced by MOLDEN.[37]

B3LYP calculation, these two components have approximately equal weights. For still larger values of R_1, beyond 2 Å, it is the aromatic character that increasingly dominates. For the unrealistically large value of R_1 obtained at the CAS(6,6) level, we find that the aromatic combination strongly dominates the total spin function, with a weight of 0.80. The total weight of the minority "bisallyl" component never exceeds 0.15 over this range of R_1.

The Cope Rearrangement of 2,5-DCH. The cyano substituents in this system are located at the nodal positions in the two allyl moieties, and so the expectation from the chameleonic model[13,18] is of a transition region that is shifted toward the cyclohexadiyl extreme. If this is indeed correct, then the SC(6) calculations should show a larger weight for the Rumer spin function 5 ≡ (1−6, 2−5, 3−4).

The B3LYP/6-31G(d)-optimized gas-phase C_{2h} TS geometry is shown in Figure 4a and features a rather short interallyl distance of 1.75 Å, as anticipated. The symmetry present in the parent reaction is preserved, due to the positions of the substituent sites. The active orbitals from the SC(6)/6-31G wave function are illustrated in Figure 4b, and the SC overlap integrals between these orbitals are reported in Table 1. For the most part, the orbitals are very similar to those for the unsubstituted system. As before, orbitals ψ_1 and ψ_6 (and similarly ψ_3 and ψ_4) correspond to the forming/breaking carbon−carbon σ bonds. The corresponding overlap integrals are slightly higher than before, 0.78 as opposed to 0.74, presumably due in large part to the shorter separations. It is the overlap integral $\langle\psi_2|\psi_5\rangle$, involving the orbitals associated with the central atoms of the two allyl moieties, which shows the largest change, decreasing in absolute value from 0.41 for the parent reaction to 0.25 in this case, despite the shorter distance.

On the whole, the differences in the orbital descriptions due to the cyano substitution appear to be fairly modest. The same is certainly not true of the active-space spin-coupling pattern, as can be seen from the Chirgwin−Coulson (P_k^{CC}) and Gal-

TABLE 1: Overlap Integrals $\langle\psi_\mu|\psi_\nu\rangle$ between the Active Orbitals from SC(6)/6-31G Wave Functions Calculated at the B3LYP/6-31G(d)-Optimized Gas-phase TS Geometries for the Cope Rearrangements of 1,5-H, 2,5-DCH, and 1,3,5-TCH[a]

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
			1,5-H			
ψ_1	1	0.287	0.134	0.141	0.101	0.739
ψ_2	0.287	1	0.287	0.101	−0.414	0.101
ψ_3	0.134	0.287	1	0.739	0.101	0.141
ψ_4	0.141	0.101	0.739	1	0.287	0.134
ψ_5	0.101	−0.414	0.101	0.287	1	0.287
ψ_6	0.739	0.101	0.141	0.134	0.287	1
			2,5-DCH			
ψ_1	1	0.277	0.093	0.090	0.143	0.782
ψ_2	0.277	1	0.277	0.143	−0.247	0.143
ψ_3	0.093	0.277	1	0.782	0.143	0.090
ψ_4	0.090	0.143	0.782	1	0.277	0.093
ψ_5	0.143	−0.247	0.143	0.277	1	0.277
ψ_6	0.782	0.143	0.090	0.093	0.277	1
			1,3,5-TCH			
ψ_1	1	0.503	0.023	−0.091	0.046	0.559
ψ_2	0.503	1	0.503	0.143	−0.100	0.143
ψ_3	0.023	0.503	1	0.559	0.046	−0.091
ψ_4	−0.091	0.143	0.559	1	0.506	0.108
ψ_5	0.046	−0.100	0.046	0.506	1	0.506
ψ_6	0.559	0.143	−0.091	0.108	0.506	1

[a] A consistent numbering scheme, as described in the text, is used for each system.

TABLE 2: Chirgwin−Coulson (P_k^{CC}) and Gallup−Norbeck (P_k^{GN}) Weights of the Rumer Spin Functions Included in the Active-Space Spin-Coupling Pattern Θ_{00}^{6} for the B3LYP/6-31G(d)-Optimized Gas-phase TS Geometries for the Cope Rearrangement of 1,5-H, 2,5-DCH, and 1,3,5-TCH

		1,5-H		2,5-DCH		1,3,5-TCH	
k	Rumer function	P_k^{CC}	P_k^{GN}	P_k^{CC}	P_k^{GN}	P_k^{CC}	P_k^{GN}
1	(1−2, 3−4, 5−6)	0.2083	0.1430	0.1280	0.0468	0.4020	0.4619
2	(1−4, 2−3, 5−6)	0.0633	0.0303	0.0107	0.0010	0.0469	0.0127
3	(1−2, 3−6, 4−5)	0.0633	0.0303	0.0107	0.0010	0.0469	0.0127
4	(1−6, 2−3, 4−5)	0.2083	0.1430	0.1280	0.0468	0.4020	0.4619
5	(1−6, 2−5, 3−4)	0.4569	0.6533	0.7227	0.9042	0.1021	0.0509

lup−Norbeck (P_k^{GN}) weights collected in Table 2. The Chirgwin−Coulson weight of the diradical component has increased from 0.46 to 0.73, with the corresponding total aromatic weight decreasing from 0.42 to 0.25. The total weight of the minority "bisallyl" component is now almost negligible. Comparison to Figure 3 shows that the weights of the Rumer spin functions for the TS of 2,5-DCH are fairly similar to the corresponding values for the parent reaction, if the TS had the same value of R_1. Our various observations from the SC(6) calculations certainly support the assertion of Staroverov and Davidson[6,17] that the diradical character of the TS for 2,5-DCH is much more dependent on the interallyl distance than on the presence of radical-stabilizing substituents.

The Cope Rearrangement of 1,3,5-TCH. In view of the different substitution patterns in the two allyl moieties, the centauric model is expected to be more appropriate than the chameleonic one.[13,18] The substituents at the active positions C1 and C3 should push the TS region toward the bisallyl extreme, whereas the cyano group at the C5 nodal position should pull it toward the cyclohexadiyl region. The B3LYP/6-31G(d)-optimized gas-phase TS geometry for the Cope rearrangement of 1,3,5-TCH is shown in Figure 5a and features a fairly large interallyl separation of 2.11 Å, as expected. Because of the asymmetric pattern of substitution, there is an obvious reduction of symmetry of the lowest-energy chairlike TS to C_s in this instance.

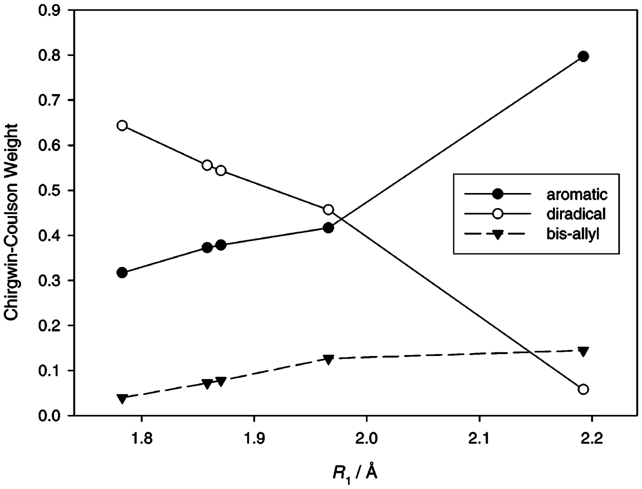


Figure 3. Composition of the active-space spin-coupling pattern Θ_{00}^{6} at different TS geometries for the Cope rearrangement of 1,5-H. "Aromatic" labels the total Chirgwin−Coulson weight of the combination 1 ≡ (1−2, 3−4, 5−6) plus 4 ≡ (1−6, 2−3, 4−5), "diradical" signifies the corresponding weight of 5 ≡ (1−6, 2−5, 3−4), and "bisallyl' relates to the minority component 2 ≡ (1−4, 2−3, 5−6) plus 3 ≡ (1−2, 3−6, 4−5).

The active orbitals of the SC(6)/6-31G wave function calculated at this geometry are shown in Figure 5b. Orbitals ψ_1 and ψ_3, which are symmetry equivalent due to the mirror plane, are located on the 1,3-dicyano fragment and closely resemble the orbitals for the other cases we have discussed. Orbitals ψ_4 and ψ_6, which are also related to one another by reflection, are located on the allyl fragment with the single cyano group, and exhibit pronounced distortions toward the central orbital on that fragment, ψ_5. Because of the reduced symmetry of the system, there are no further symmetry relations between the orbitals, and this leads to many more unique overlap integrals, as reported in Table 1. For the other systems considered, the overlap integrals in the forming/breaking carbon−carbon σ bonds, $\langle\psi_1|\psi_6\rangle$ and $\langle\psi_3|\psi_4\rangle$, exceeded 0.7. In 1,3,5-TCH, these values have dropped significantly to 0.56, which is not very different from the nearest-neighbor overlaps, $\langle\psi_1|\psi_2\rangle$, $\langle\psi_2|\psi_3\rangle$, $\langle\psi_4|\psi_5\rangle$, and $\langle\psi_5|\psi_6\rangle$, which are all close to 0.5. The corresponding values for 1,5-H and 2,5-DCH were approximately 0.3. Thus, compared to the other systems, 1,3,5-TCH appears to show a significant move toward equalization of nearest-neighbor overlaps. Such observations are the first hint of increased aromatic character in the TS for this system. For confirmation we need to look, of course, at the coupling of the electron spins.

Chirgwin−Coulson (P_k^{CC}) and Gallup−Norbeck (P_k^{GN}) weights of the Rumer spin functions included in the active-space spin-coupling pattern Θ_{00}^{6} are given in Table 2. The two symmetry-equivalent Kekulé modes give a total "aromatic" Chirgwin−Coulson weight of 0.80, whereas the corresponding value for the "diradical" component is now just 0.10. The two remaining "bisallyl" modes account for the remaining 0.09. The spin function weights, taken together with the form of the active orbitals and the overlaps between them, suggest that the Cope rearrangement of 1,3,5-TCH passes through a TS that can be considered to be strongly aromatic, with benzene-style resonance between two Kekulé-type Rumer spin functions.

Of course, in line with the notion that the radical character of the TS is not much altered by the presence of radical-stabilizing substituents, but depends mainly on the interallyl

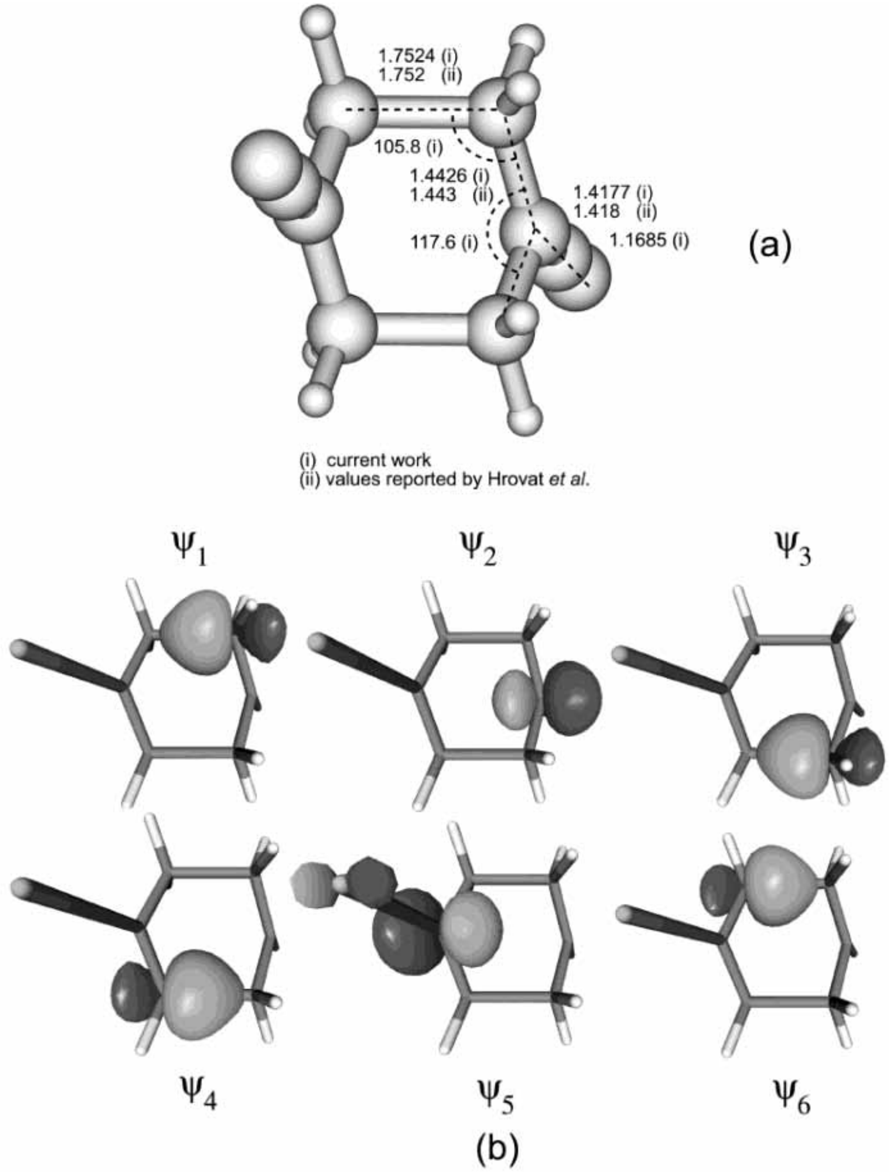


Figure 4. (a) B3LYP/6-31G(d) geometry for the gas-phase TS of the Cope rearrangement of 2,5-dicyano-1,5-hexadiene, with bond lengths in angstroms and angles in degrees. (b) Active orbitals from SC(6)/6-31G calculations at this geometry, represented in the same fashion as in Figure 2.

distance,[6,17] the separation of 2.11 Å for 1,3,5-TCH should indeed result in much more aromatic character than for 1,5-H and 2,5-DCH.

The Cope Rearrangement of 1,3,4,6-TeCH. This system features equivalent substitution in the two allyl moieties, with all of the cyano groups located in the active positions. According to the chameleonic model,[13,18] we can expect a strong bias toward the extreme of two noninteracting allyl radicals.

The lowest-energy "chair" B3LYP/6-31G(d)-optimized TS geometry for the gas-phase Cope rearrangement of 1,3,4,6-TeCH is shown in Figure 6a, and the corresponding active orbitals from the SC(6)/6-31G wave function are displayed in Figure 6b. Analogous calculations on the isolated allyl radical[34] yield SC orbitals that resemble in- and out-of-phase combinations of deformed p_π functions on the terminal carbon atoms, with the corresponding spins approximately triplet coupled. Such a description has been labeled an "antipair solution".[34−36] The remaining valence π orbital in the allyl radical is mostly associated with the central carbon atom. It is clear from Figure 6b that the shapes of the active orbitals for the TS of 1,3,4,6-TeCH correspond essentially to antipair solutions in each allyl moiety. This is confirmed by examining the corresponding SC overlap integrals (see Table 3) and the active-space spin function, which is dominated by almost exactly triplet coupling of the spins associated with ψ_2 and ψ_3 as well as with ψ_5 and ψ_6. Such a solution arises due to the very large interallyl separation of 2.467 Å. We note that an analogous antipair SC(6) solution was obtained[19] for the Cope rearrangement of 1,5-H when examining the higher-energy C_{2v} "boat" TS at the geometry predicted at just the CAS(6,6)/6-31G(d) level ($R_1 =$ 2.545 Å). However, higher-level calculations on the "boat" TS for the 1,5-H rearrangement again indicate a somewhat shorter interallyl distance,[7,20] with probably the most reliable estimate being 2.193 Å,[20] at which the antipair description is unlikely to present a viable alternative to the solution with localized orbitals.

Summary and Conclusions

By use of gas-phase transition-state geometries for the Cope rearrangements of 1,5-H and of various cyano derivatives, taken from appropriate B3LYP/6-31G(d) optimizations, ab initio modern VB calculations have been used to quantify directly

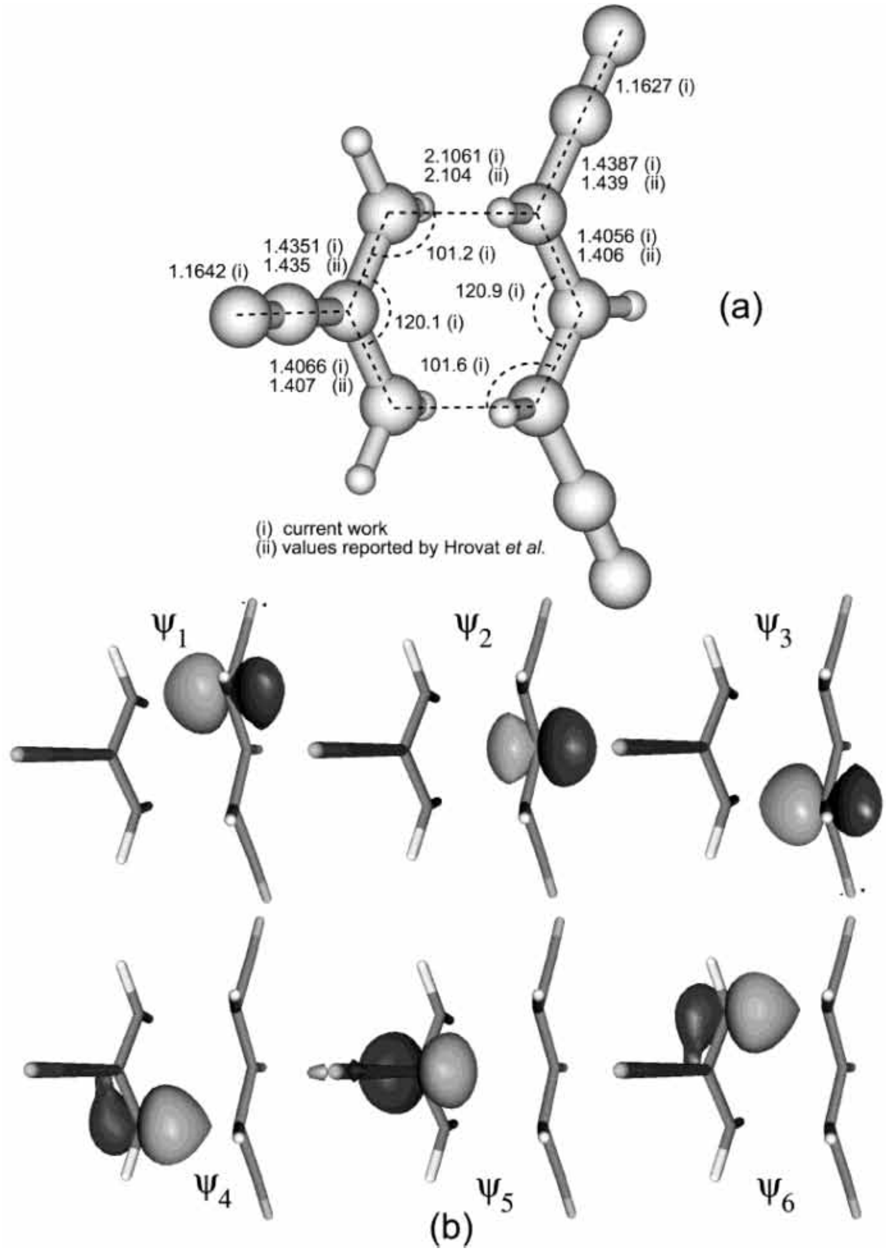


Figure 5. (a) B3LYP/6-31G(d) geometry for the gas-phase TS of the Cope rearrangement of 1,3,5-tricyano-1,5-hexadiene, with bond lengths in angstroms and angles in degrees. (b) Active orbitals from SC(6)/6-31G calculations at this geometry, represented in the same fashion as in Figure 2.

the relative importance of aromatic, diradical, and bisallyl contributions. Further information is provided by the forms of the active-space orbitals and, in particular, by the overlaps between them. Of course, similar analysis performed at geometries taken from CAS(6,6) optimizations would not have been meaningful because of the particular sensitivity of the potential-energy hypersurfaces to the inclusion of dynamic electron correlation.

The chameleonic TS of 2,5-DCH features a somewhat shorter interallyl distance than does the parent reaction, but the shapes of the active SC orbitals turn out to be rather similar. In terms of overlap integrals, the largest change is in $\langle\psi_2|\psi_5\rangle$, involving the orbitals associated with the central atoms of the two allyl moieties; this shows a significant decrease in absolute value, despite the shorter distance. We attribute this behavior to the effect of the electron-withdrawing cyano groups attached to the carbons hosting ψ_2 and ψ_5.

Contrary to expectations in some of the literature, we find that the TS for the parent reaction is not predominantly aromatic. Instead, the interallyl separation of ca. 1.97 Å is in the region for which the weights of the aromatic and diradical components are almost equal. The somewhat shorter separation for the 2,5-DCH TS (ca. 1.75 Å) is reflected in a large increase in the weight of the diradical character at the expense of the aromatic modes.

The larger interallyl separation of ca. 2.11 Å in the case of the TS for 1,3,5-tricyano-1,5-hexadiene is reflected in significant equalization of nearest-neighbor active-orbital overlaps, including those for the forming/breaking carbon−carbon σ bonds. This is accompanied by a large increase in the total weight of the aromatic active-space spin-coupling component, which becomes dominant.

It is clear from results for these systems that the main effect on the character of the TS of substituting radical-stabilizing

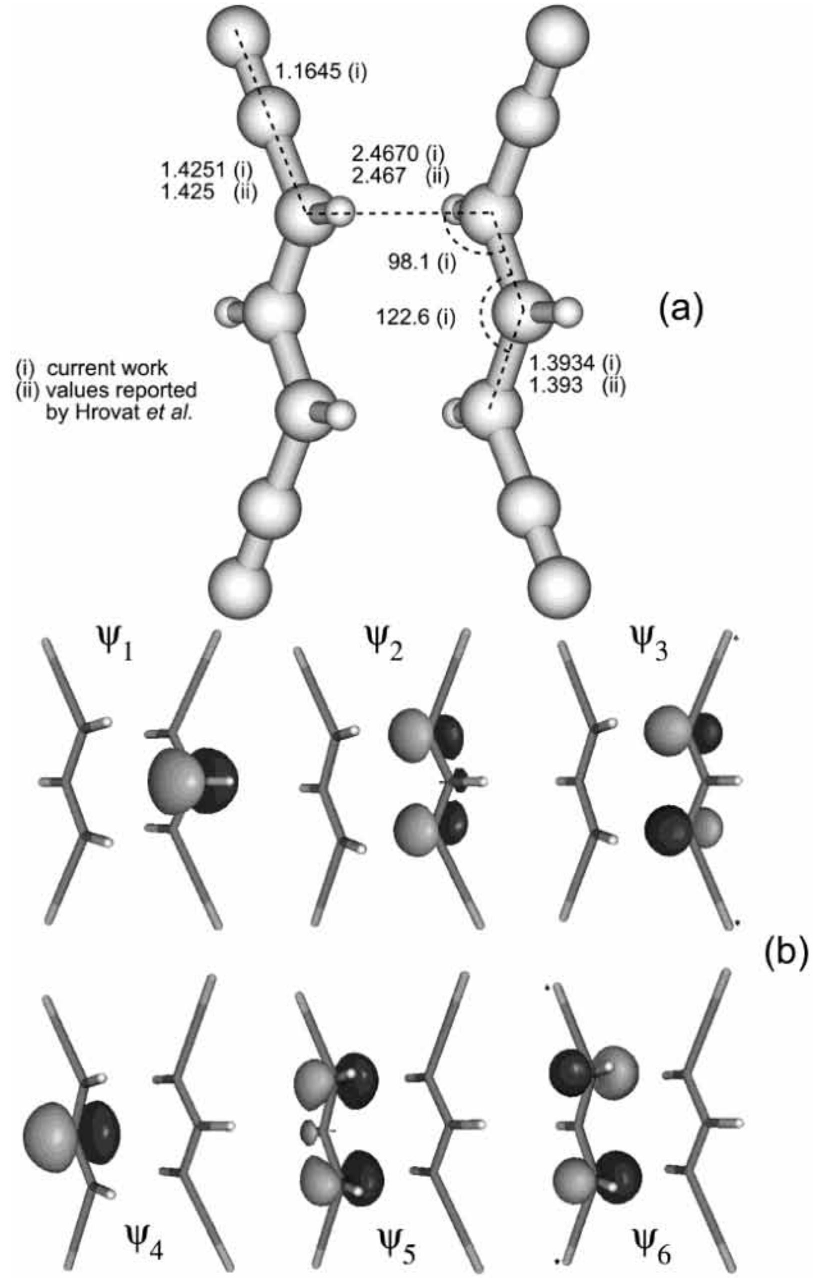


Figure 6. (a) B3LYP/6-31G(d) geometry for the gas-phase TS of the Cope rearrangement of 1,3,4,6-tetracyano-1,5-hexadiene, with bond lengths in angstroms and angles in degrees. (b) Active orbitals from SC(6)/6-31G calculations at this geometry, represented in the same fashion as in Figure 2.

TABLE 3: Overlap Integrals $\langle\psi_\mu|\psi_\nu\rangle$ between the Active Orbitals from SC(6)/6-31G Wave Functions Calculated at the B3LYP/6-31G(d)-Optimized Gas-phase TS Geometries for the Cope Rearrangement of 1,3,4,6-TeCH[a]

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
ψ_1	1	0.730	0.000	−0.113	−0.147	0.000
ψ_2	0.730	1	0.000	−0.147	−0.248	0.000
ψ_3	0.000	0.000	1	0.000	0.000	0.505
ψ_4	−0.113	−0.147	0.000	1	0.730	0.000
ψ_5	−0.147	−0.248	0.000	0.730	1	0.000
ψ_6	0.000	0.000	0.505	0.000	0.000	1

[a] The orbitals are numbered as shown in Figure 6.

cyano groups is in fact indirect via the geometry. In essence, short interallyl separations favor diradical character and larger ones favor aromaticity. Further support for this simple observation comes from analyzing the 1,5-H active-space spin functions for TS geometries optimized at different levels of theory. Changes in the TS interallyl distance between 1.75 and 2.2 Å, whether due to cyano substitution or (artificially) by changing the level of theory, leads mostly to a gradual switch between the diradical and aromatic character. The weight of the bisallyl component does become slightly more important for the larger interallyl distances in this range, but it still remains fairly small. Only for the much larger distance of ca. 2.47 Å in the case of 1,3,4,6-tetracyano-1,5-hexadiene did we observe a significant bisallyl contribution. This large-separation case turns out to have predominantly bisallyl spin character, alongside an orbital description that resembles that of two separate allyl radicals.

References and Notes

(1) Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213.

(2) Rhoads, S. *Molecular Rearrangements*; Wiley: New York, 1963; Vol. 1.

(3) Gajewski, J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981.

(4) Dewar, M. J. S.; Jie, C. *Acc. Chem. Res.* **1992**, *25*, 537.

(5) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378.

(6) Staroverov, V. N.; Davidson, E. R. *THEOCHEM* **2001**, *573*, 81. Staroverov, V. N.; Davidson, E. R. *THEOCHEM* **2002**, *617*, 225.

(7) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

(8) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.

(9) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(10) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

(11) Davidson, E. R. *J. Phys. Chem.* **1996**, *100*, 6161.

(12) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529.

(13) Doering, W. v. E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10112.

(14) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

(15) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.

(16) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 186.

(17) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 7377.

(18) Doering, W. v. E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10967.

(19) Oliva, J. M.; Gerratt, J.; Karadakov, P. B.; Cooper, D. L. Unpublished work. Oliva, J. M. *Theor. Chem. Acc.* **1999**, *103*, 1.

(20) Ventura, E.; do Monte, S. A.; Dallos, M.; Lischka, H. *J. Phys. Chem. A* **2003**, *107*, 1175.

(21) Sakai, S. *THEOCHEM* **2002**, *583*, 181.

(22) Blancafort, Ll.; Celani, P.; Bearpark, M. J.; Robb, M. A. *Theor. Chem. Acc.* **2003**, *110*, 92.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(25) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.

(26) Karadakov, P. B.; Cooper, D. L.; Gerratt, J. *J. Am. Chem. Soc.* **1998**, *120*, 3975.

(27) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979.

(28) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1992**, *97*, 7637.

(29) Kotani, M.; Amemyia, A.; Ishiguro, E.; Kimura, T. *Tables of Molecular Integrals*; Maruzen: Tokyo, 1963.

(30) Rumer, G. *Göttinger Nachr.* **1932**, *3*, 337.

(31) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Theor. Chim. Acta* **1995**, *90*, 51.

(32) Chirgwin, B. H.; Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1950**, *201*, 196.

(33) Gallup, G. A.; Norbeck, J. M. *Chem. Phys. Lett.* **1973**, *21*, 495.

(34) Oliva, J. M.; Gerratt, J.; Cooper, D. L.; Karadakov, P. B.; Raimondi, M. *J. Chem. Phys.* **1997**, *106*, 3663.

(35) Wright, S. C.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc. Chem. Commun.* **1989**, 1489. Wright, S. C.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Phys. Chem.* **1992**, *96*, 7943. Raos, G.; McNicholas, S. J.; Gerratt, J.; Cooper, D. L.; Karadakov, P. B. *J. Phys. Chem. B* **1997**, *101*, 6688.

(36) Karadakov, P. B.; Gerratt, J.; Raos, G.; Cooper, D. L.; Raimondi, M. *J. Am. Chem. Soc.* **1994**, *116*, 2075.

(37) Schaftenaar, G. *MOLDEN (A Pre- and Postprocessing Program of Molecular and Electronic Structure)*; CAOS/CAMM Center: The Netherlands.